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ON THE POSSIBILITY OF QUANTITATIVE ASSAY OF HYDRAZINE, ITS SPLITTING PRODUCTS, AND ITS IMPURITIES

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ON THE POSSIBILITY OF QUANTITATIVE ASSAY OF HYDRAZINE, ITS SPLITTING PRODUCTS, AND ITS IMPURITIES

PART I - UTILIZATION OF GAS CHROMATOGRAPHY IN MONITORING THE ACTIVITY LEVEL OF HYDRAZINE BREAKDOWN CATALYSTS

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A gas chromatography method is proposed for performing a quantitative assay of hydrazine and its usual splitting products, N_2, NH_3 and H_2. With one of the columns, adapted for polar substances, water can also be assayed.

This method can be used both for monitoring the activity level of catalysts undergoing breakdown, as well as for investigating reaction stoichiometrics. It can also be employed in studying the hydrazine breakdown kinetics in the heterogeneous phase.

The method is based on the use of two switchable gas chromatography columns; water and hydrazine are assayed on one nitrogen and amonia on the other. Since hydrogen is generated by the splitting of hydrazine, it is assayed by a differential calculation from the known conversion patterns of hydrazine, after having settled the matter of the nitrogen balance. It has no influence on the nitrogen assay, since hydrogen is always employed as carrier gas.

The method in question has been used for a check-up of the hydrazine break-down reaction stoichiometrics on some laboratory made catalysts.

Introduction:

Utilization of hydrazine as a missile-propellant has been growing in importance owing to its hypergolicity with many oxydizing substances and the possibility of using it as a monopropellant.

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This latter possibility is due to the ease with which hydrazine can be broken down on suitable catalysts, yielding NH_3, N_2 and H_2 in accordance with the following two successive reaction stages:

$$3\ N_2H_4 \longrightarrow 4\ NH_3 + N_2 + 36{,}360\ \text{kcal}$$

$$4\ NH_3 \longrightarrow 2\ N_2 + 6\ H_2 + 19{,}960\ \text{kcal}.$$

Breakdown in the homogeneous phase is relatively slow and therefore requires rather large combustion chambers, a fact which is scarcely in keeping with the auxiliary propulsion for which monopropellant hydrazine is intended.

Recent discovery of spontaneous splitting catalysts [1] augurs well for reduction of combusion - chamber size, so that it has become possible to contemplate using monopropellant hydrazine in directional-adjustment rockets thanks to greatly reduced size and practical and fail-safe functioning.

From all the foregoing it can be seen how important it is to have available methods for preliminary laboratory estimates of the catalytic level of activity of substances to be used in rocket-engine experiments. For this purpose we can make use of methods already widely-employed in monitoring the activity level of industrial catalysts, such as the flow method [2] and the more modern pulse-chromatography method [3]. The latter method is especially recommended owing to the rapidity of the responses as well as the slight quantity of hydrazine that it requires. In both cases, it is indispensable to have available an efficient and practical quantitative method of assaying N_2H_4 (for verification of conversion patterns), NH_3, N_2 and H_2, as well as any impurities the starting hydrazine might contain.

These impurities can have considerable influence on breakdown velocity [4] [5].

In the present study, we have attempted to satisfy simultaneously all these requirements by using the gas chromatography method and trying to combine quantitative assay of impurities with monitoring of the activity level of breakdown catalysts.

Solution of the quantitative problem connected with hydrazine will have considerable bearing on studies of breakdown in the homogeneous phase as well as industrial processes involving production or dishydration of hydrazine.

ASSAY OF EVER-PRESENT

IMPURITIES IN HYDRAZINE

Water and ammonia are ever-present impurities in hydrazine. As a rule a suitable concentration of water, which can be separated from hydrazine only with some difficulty [6], is expressly left in the commercial product on account of its stabilizing action and the fact that it considerably lowers the freezing point of hydrazine, with the result that hydrazine can also be used at low temperatures (cf. anhydrous hydrazine at]°C, [6].

Ammonia on the other hand, is one of the splitting products of hydrazine and, in veiw of the instability of hydrazine, is always present.

Numerous are the gas-chromatography methods that have been proposed for separation of hydrazine and water [7], [8], [9], [10], [11], [12], [13], because this separation entails a difficulty of choice of columns adapted for the strong polarity of both components.

Nevertheless, it is evident from the literature that, after several unsuccessful tries, the chromatography column of G.D. Lakata [12], which uses trietanolammine as the distribution fluid and acid-washed chromosorb W as the support, turned out to be the best, giving rise to almost symmetirical and well-separated peaks.

L. A. Dee and A. K. Webb [13] have suggested using 2-hydrazine pyradine as the stationary phase, but the low stability of this substance is an inconvenience which even the authors themselves recognize.

On the analogy of the experiements carried out on alifatic amines by Y. L. Sze, M. L. Borke, and D. M. Ottenstein [14], in the course of the present study, we thought that the utilization of trietanolammine as the distribution fluid could be improved by addition of tetraetilenpentammine.

Peak symmetry does indeed improve considerably, but the concentration of tetraetilenpentammine has got to be kept below certin levels; otherwise we no longer obtain a good separation.

The gas-chromatography assay of water in hydrazine is sufficiently precise only for quantities greater than 0.5 : 1% in weight.

This low precision is due to the low response of the detector which most of the time must be used at its highest sensitivity, and to the high hygroscopicity of hydrazine. This latter reason, as a matter of fact, explains why it is always difficult to proceed in such a manner that the injected sample does not absorb at least some humidity.

On the other hand, not many other methods are available. The method of Karl Fisher is not applicable because of its numerous side effects, while the differential spectrometry method [15], which uses the absorption band of water at 1.9 micron, demands exceptional purity of the reference sample. The classical method of R. A. Penneman and L. F. Audrieth [16] would have us combine a touch of iodometry for the hydrazine with an acidimetry that assays the amount of alkilinity due to the $N_2 H_4 + NH_3$. Then the water could be assayed by differential calculation. This method, however, while it is satisfactory for assaying the quantity of hydrazine, gives no guarantee of certainty in assaying the water.

The method proposed recently [17] for potentiographic assay of water in hydrazine by one of the A.A's, based on the following reaction conducted in the hydrazine solvent:

$$NaN_2H_3 + H_2O \longrightarrow NaOH + N_2H_4 ,$$

while it does solve the problem of assaying water directly and with precision, is far too slow on account of the numerous precautions required in handling sodium hydrazide solutions in hydrazine. Besides, it must be combined with other methods for assaying hydrazine. The gas-chromatography method, therefore, retains its importance on account of the rapidity and convenience by which it is characterized.

As regards the ammonia, there are to be found in the literature gas-chromatography methods for separation of alipatic amines of low molecular weight [14]. Other gas-chromatography methods for separation of ammonia are cited by Jeffery and Kipping [18]. The method proposed by R. W. Jenkins, C. H. Check and Y. J. Linnenbaum [19] is not applicable in the present case because the hydrazine interferes. The gas-chromatography assay of ammonia in hydrazine is not convenient if the ammonia is present in small quantities owing to the low response of the detector. Consequently, we do not recommend this method for assay of ammonia as an impurity in hydrazine. This problem can, as a matter of fact, be solved more brillantly by the quantitative method proposed in Part II of the present study, to which we refer the reader for more detailed discussion.

ASSAY OF HYDRAZINE AND ITS SPLITTING PRODUCTS - MONITORING THE ACTIVITY LEVEL OF CATALYSTS UNDERGOING BREAKDOWN

A quantitative method for assaying N_2H_4, NH_3, N_2 and H_2 has been suggested by B. E. Knox and E. T. McHale [20]. This method, however, is of rather limited application and not very adapted to our purpose. Other quantitative methods employed in the course of particular studies resort to the use of more than one quantitative instrument for monitoring each of the substances to be separated and do not concern themselves with the problem of monitoring catalytic activity.

In the present study, the problem was confronted and solved using two switchable gas-chromatography columns, one of which was adapted for separation of H_2O and N_2H_4 and the other, for separation of N_2 and NH_3. Inasmuch as hydrogen is generated by the splitting of hydrazine, it can be assayed by a differential calculation from the known conversion patterns of hydrazine after having settled the matter of the nitrogen balance. It has no influence on the nitrogen assay inasmuch as the hydrogen itself is used as the carrier gas.

Utilization of the gas-chromatography method, which was not very convenient for assaying ammonia as an impurity in hydrazine, does become so when the hydrogen is generated by the catalytic splitting of hydrazine.

In this particular case, it is necessary, as we have already stated, to employ a column adapted for separation of N_2 and NH_3. For this purpose, we found satisfactory the use of columns of 100-120 mesh Porapak T with trietanolammine as the stationary phase.

In this connection, let us recall how Porapak is constituted of porous polymers obtained by polymerization in suspension of stirol and divinilbenzol as reticulation agent [21]. Generally, these polymers can function simultaneously as solid support and stationary phase. In the case of ammonia, however, as in the case of the ammines too, it is advisable, in order to reduce absorption, to impregnate the Porapak with a suitable distribution fluid that has the function of eliminating all residual activity of the solid support. Very suitable for this purpose are trietanolammine and tetraetilenpentammine.

We achieved monitoring of catalytic activity by placing a small catalytic bed inside the thermostatization chamber. If need be, this catalytic bed can be protected from the flow of carrier gas.

Experimental Part

A) Preliminaries

The problem of separation of N_2, NH_3, N_2H_4, H_2O and H_2 that arises in monitoring the activity level of catalysts for spontaneous splitting of hydrazine, in view of the different kinds of substances to be analyzed, was solved by using, as we have already indicated, two gas-chromatography columns, one of which was adapted for separation of N_2H_4 and H_2O and the other, for separation of N_2 and NH_3. Inasmuch as hydrogen is generated by the splitting of hydrazine, it can be assayed by a differential calculation from the known conversion patterns of hydrazine after having settled the matter of the nitrogen balance. It has no influence on the nitrogen assay inasmuch as the hydrogen itself is used as the carrier gas.

Immersed in the same thermostatic chamber, both columns function at the same temperature and under the same flow conditions, which simplifies utilization as well as interpretation of the results. The columns are connected through an externally-controlled device that allows the carrier gas to be passed into either column as required.

A complete analysis for monitoring the activity level of a catalyst for hydrazine breakdown can be carried out in three stages. In the first stage, we inject a known quantity of hydrazine directly onto the column for the N_2H_4 and H_2O (Fig. 1a). In the second stage, we inject the same quantity through a catalytic bed of suitable size inserted before the column (Fig. 1b). From the ratio between the areas of the peaks, we calculate the conversion patterns of hydrazine.

In the third stage, after having switched columns, we inject the same quantity of hydrazine through the catalytic bed. In this way, we separate the N_2 and NH_3 (Fig. 1c). If Q = quantity of hydrazine injected in the correct weight for absorption on the catalyst and c = conversion in weight % : 100, then

$$Qc = q_{NH_3} - q_{N_2} - q_{H_2} .$$

In this equation, all the terms are known except q_{H_2}, which can be assayed by a differential calculation. The experiments reported in Fig. 1b and 1c are relative to a catalytic bed of 0.5 cm of CNPM-A4 catalyst. Placed in a 0.6 cm-diameter inox steel tube in the same thermostatic chamber in which the gas-chromatography columns are located, this catalytic bed can be protected from the flow of carrier gas by means of a suitable externally-controlled valve.

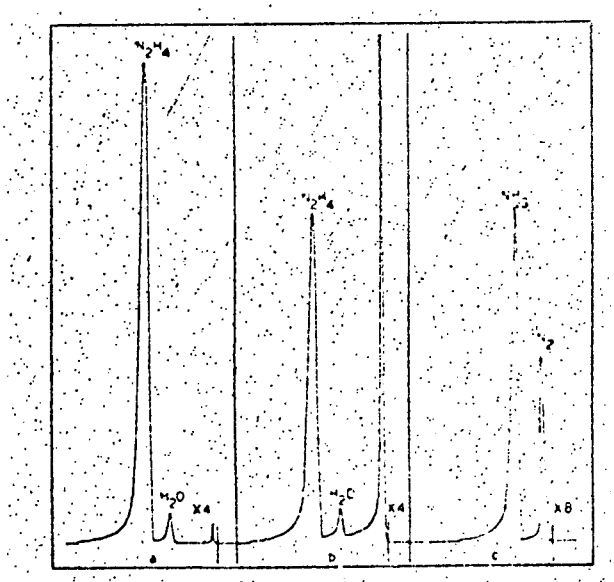
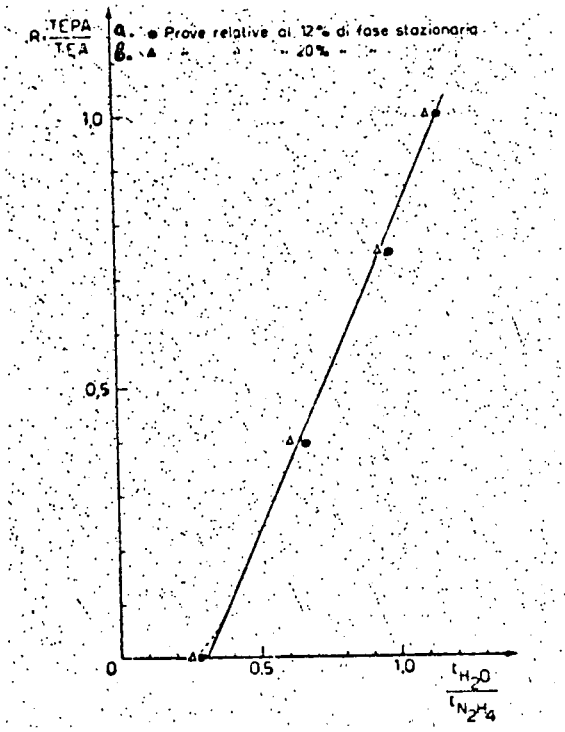


Fig. 1 - a. Typical chromatogram for hydrazine-water on column B (see Table 1). Injected sample=10 µl. Recording velocity=10 mm/min.
b. Chromatogram also recorded on column B with 10 µl of hydrazine after passage on breakdown catalyst.
c. Chromatogram registered for hydrazine splitting products on 100-120 mesh Porapak T column after passage on the same catalyst as above.



a. Tests relative to 12 % of stationary phase
b. Tests relative to 20 % of stationary phase

Fig. 2 - Peak resolution of H_2O and N_2H_4 as a function of the ratio of TEPA/TEA.

B) Preparation of the Column for Separation of N_2H_4 and H_2O

We tested many gas-chromatography columns, now varying the support, now the distribution fluid. In the end, we settled in favor of using 2 meter-long by 0.6 cm-diameter inox steel columns filled with acid-washed, 30-60 mesh Chromosorb W and, as distribution fluid, a mixture of trietanolammine and tetraetilenpentammine.

More exactly, we conducted tests using trietanolammine alone and mixtures of T.E.P.A. and T.E.A. in various proportions, using both the T.E.A. and the T.E.P.A./T.E.A. mixtures at 12% in weight relative to the support and, in other tests, at 20%. The peaks obtained in the case of T.E.P.A./T.E.A. mistures are satisfactorily symmetrical (Table I).

Then we conducted a critical examination to determine the best T.E.P.A./T.E.A. ratio. We found that by increasing the quantity of T.E.P.A. we obtain for a 1-to-1 ratio in moles absolute inversion of the emergence order of the peaks for water and hydrazine (Fig. 2) with bad resolution.

This means that we can improve separation as well as symmetry by varying the T.E.P.A./T.E.A. ratio. In our case, we found satisfactory a T.E.P.A./T.E.A. ratio in moles of 2/5.

The support was impregnated by dissolving the distribution fluid in methanol, mixing this solution with a weighed quantity of support and then evaporating the solvent in an oven at 60° C under agitation.

Results Obtained

Some of the results we obtained with different columns are shown in Table I. The results obtained with the column of T.E.P.A./T.E.A. = 2/5 for five standard H_2O - N_2H_4 samples are given in Table II. These samples were prepared by adding weighed quantities of water to absolutely anhydrous hydrazine [17]. Corrections were made by the internal normalization method.

The linearity experiments for this column for water as well as hydrazine gave good results and absorbtion can be safely disregarded (Fig. 3). In view of the low response of the detector, when assaying small quantities of water, it is necessary to set the instrument for highest sensitivity. We also tested columns with teflon as solid support. The improvement in the results, however, does not compensate for the difficulties encountered in filling the column.

Table 1

TABELLA I

Column Colonne	$R = \frac{\text{T.E.P.A.}}{\text{T.E.A.}}$	% in weight stationary phase	Retention time *		Symmetry factor **	
			H_2O	N_2H_4	H_2O	N_2H_4
A	0	12	57	210	1,26	1,52
B	2/5	12	121	183	1,06	1,10
C	3/4	12	135	141	1,06	1,09
D	1/1	12	149	129	1,05	1,09
E	0	20	129	491	1,22	1,41
F	2/5	20	285	473	1,00	1,06
G	3/4	20	326	347	1,02	1,05
H	1/1	20	368	330	1,00	1,03

* Retention times were corrected by subtracting the time the gases took to pass throught the column

** Calculated according to Dal Nogare Chiu (31) $A_s = \frac{x - y}{(x-y) - (y-x)}$

Table 2

Tests	Composition% in wt		N_2H_4 found	H_2O found	% error for N_2H_4	% error for H_2O
	N_2H_4	H_2O				
1	97,02	2,94	96,91	2,96	— 0,11	+ 0,61
2	94,15	5,84	94,03	5,82	— 0,13	— 0,34
3	85,13	14,86	84,65	14,76	— 0.56	— 0,67
4	73,02	26,95	73,00	26,84	— 0,02	— 0,41
5	63,16	36,82	63,24	36,61	+ 0,12	— 0,57

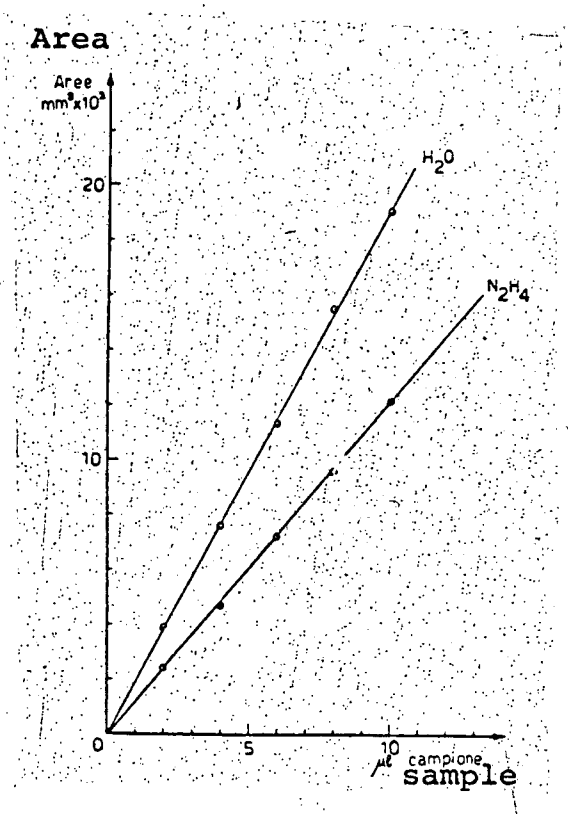


Fig. 3 - Linearity test for H_2O/N_2H_4.

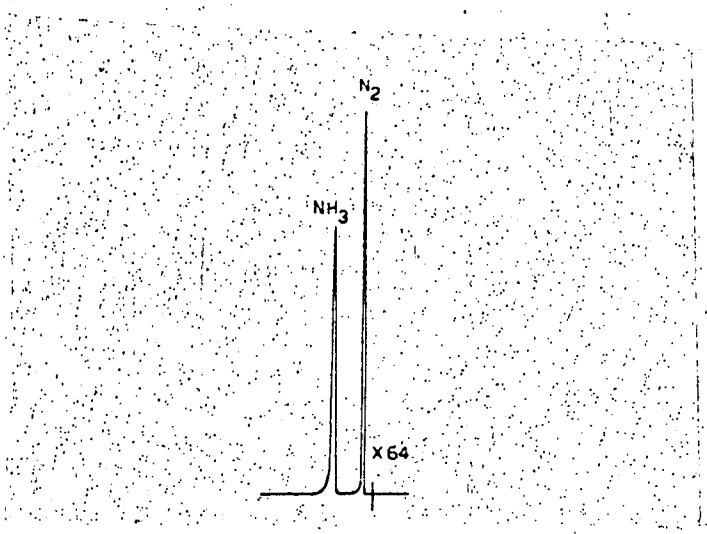


Fig. 4 - Typical chromatogram for separation of N_2/NH_3 on 100-120 mesh Porapak T with 10 % of T.E.A.

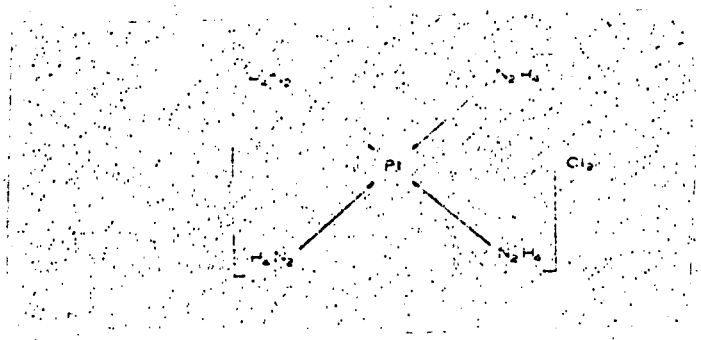
C) Preparation of the Column for Separation of N_2 and NH_3, and Results Obtained

For this column, still in a 1 meter-long by 0.6 cm-diameter inox steel tube, we resorted to a rather fine granulometry support such as 100-120 mesh Porapak T treated with 10% of T.E.A. or with T.E.P.A. In this case, the distribution fluid, as we have already stated, has the function of reducing the absorbtion of ammonia. The fine granulometry enhances the efficiency of the column, resulting in a distinct separation between N_2 and NH_3 (Fig. 4). The linearity of response for both substances is quite good. The column was prepared by dissolving the distribution fluid in methanol and mixing the resultant solution with a weighed quantity of Porapak T.

Dessication was effected in an oven at 60° C under agitation. Standardization tests were carried out on three mixtures of known NH_3 and N_2 composition. The gas samples for linearity and for the standardization tests were gotten with a 3 cm^3 sampler.

D) Preliminary Tests on Breakdown Catalysts

Catalysts that have a high activity level in hydrazine breakdown are metals with an incomplete d substratum [22] [23], and one of the stages of the breakdown mechanism consists in the formation of bonds between the nitrogen atoms of the hydrazine and the incomplete d orbitals with successive reaction [22]. Indeed, it is well known that hydrazine can give rise to compounds with different elements, like for example the following [24]:



From the practical point of view, hydrazine catalysts can be divided into spontaneous and non-spontaneous catalysts accordingly as they do instantaneously trigger the breakdown reaction at the ambient temperature or do not. It will be obvious that only spontaneous or quasi-spontaneous catalysts can find practical application in splitting chambers for monopropellant hydrazine intended for directional-adjustment rockets. This explains the importance of laboratory monitoring, in low-temperature experiments, the activity level of

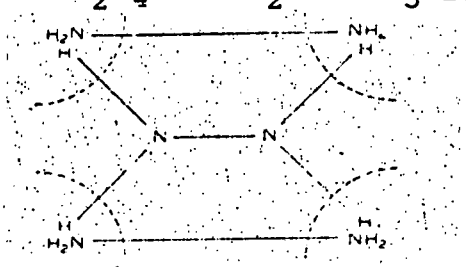
catalysts deemed to be spontaneous. Moreover, since hydrazine breakdown is an exothermic process, in order to have quantitative data for comparison, it is necessary to work under conditions of catalytic-bed isothermicity. These conditions were respected in our pulse-chromatography experiments with laboratory-made catalysts. In the course of these experiments, we observed a discrete absorbtion of hydrazine on the catalyst which was evaluated by injecting different quantities of hydrazine on the catalytic bed (Fig. 5). This absorbtion strengthens the hypothesis of formation of bonds between the nitrogen atoms of hydrazine and the d orbitals of the transition elements present in the catalyst.

The linearity of response for the different components, as can be seen from Fig. 5, gives us assurance of catalytic-bed isothermicity during the reaction.

Under the operating conditions described in Section E below, our experiments on 0.5 cm of catalytic bed in a 0.6 cm-diameter inox steel tube for CNPM-A1, CNPM-A2, CNPM-A3, CNPM-A4 and other, similar catalysts yielded the following reaction stoichiometrics:

$$1.00\ N_2H_4 \longrightarrow 1.33\ NH_3 \text{ —— } 0.33\ N_2$$

For greater assurance, we wanted to test for the absence of hydrogen using the same gas-chromatography method [25], and in practice we could find no traces of it. In view of the low temperature at which we operated (80° C) and the rather brief contact times, the stoichiometrics we came up with are understandable and in agreement with the studies of J. C. Elgin and H. S. Taylor [26], P. J. Askey [27] and especially M. Szware [28]. The last-named investigator suggests for the $3N_2H_4 \longrightarrow N_2 + 4NH_3$ reaction the following mechanism:



resulting from association of the hydrazine molecules on the catalytic surface.

Many, however, are the uncertainties about the real behavior of hydrazine undergoing breakdown in the heterogeneous phase. The breakdown mechanism probably differs for different operating conditions and different catalysts.

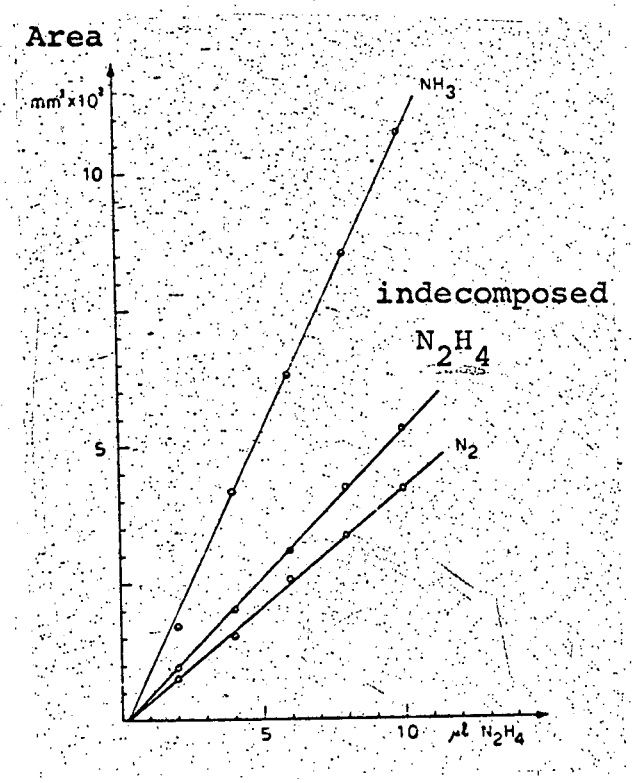


Fig. 5 - Linearity of response for N_2, NH_3, and indecomposed N_2H_4, after injection of different quantities of N_2H_4 onto a catalytic bed.

The previously cited reactions:

$$3\ N_2H_4 \longrightarrow N_4 + 4\ NH_3$$

$$4\ NH_3 \longrightarrow 2N_2 + 6\ H_2$$

are valid only as a simplified schema for rocket engines. We cannot indeed exclude the occurrence in practice of different types of breakdown like for example:

$$2\ N_2H_4 \longrightarrow H_2 + N_2 + 2\ NH_3$$

which takes place on platinum and tungsten [2] or

$$3\ N_2H_4 \longrightarrow 2\ NH_3 + 2\ N_2 + 3\ H_2$$

which occurs on Ni-Raney [22]. At the present time, therefore, no single treatment of the problem is possible. On the other hand, it can safely be said that the reaction:

$$3\ N_2H_4 \longrightarrow N_2 + 4\ NH_3$$

is favored at low temperature by the low activation energy and has a course of the first order. In effect, 10 µl of hydrazine injected into the catalytic bed at different speeds give a practically constant peak for indecomposed hydrazine [2].

At constant temperature and gas flow, therefore, the reaction velocity can be expressed as follows:

$$\frac{d[N_2H_4]}{d\ l} = K[N_2H_4]$$

If we assume that reaction time equals contact time, with easy steps we can arrive at the expression for the specific reaction velocity:

$$K = \frac{V}{LA\Theta} \ln \left(\frac{1}{1 - a} \right)$$

where

V = flow velocity in cm^3/sec

A = transversal area of bed in cm^2

L = length of bed in cm

θ + fraction of vacuum in cm^3/cm^3

a = degree of breakdown

The specific reaction velocity is the most suitable parameter for representing catalytic activity.

E) Operating Conditions, Apparatuses Used and Reagents

For our experiments we used a Carlo Erba Fractovap B gas chromatograph with a thermistor detector.

We worked with a column temperature of 80° C $\pm$ 0.2° C, while the flow of the hydrogen used as carrier gas was regulated by maintaining deliveries in the two columns at 565 cm^3/min. The deliveries were measured with a soap-film fluxometer.

The vaporizer temperature was kept at 160° C. In order to avoid thermic breakdown of the hydrazine, which takes place all too readily, it is important not to let the vaporization chamber temperature mount excessively.

The current at the thermistors was kept at 17 mA. It was then observed that the inox steel of the columns is without catalytic action on hydrazine breakdown. The arrangement for switching from one column to the other is one of the normal accessories of the apparatus.

All the reagents we used were of the highest degree of purity and came from Carlo Erba. The gases, which came from SIO, were also of the highest degree of purity, and were made to pass through molecular-sieve columns for further purification.

The absolutely anhydrous hydrazine used in preparing standard samples were laboratory-made by methods suggested by the literature [29] [30] [17], subjecting the hydrate hydrazine to three successive distillations, the first on CaO, the second on BaO and the last, after having eliminated every trace of water with sodium hydrozide as described in a previous work [17], under a vacuum, eliminating distillation heads and tails.

The injections into the G. C. were made with a 10 µℓ Hamilton microsyringe.

In the case of assay, for the check-up of the reaction stoichiometrics on catalysts, which requires that we know with precision the quantity of hydrazine injected, we proceeded with the utmost accuracy.

We realize that, despite all precautions, injection of a certain volume of fluid is not very precise and reproducible owing to the evaporation of that part of the fluid which remains in the needle of the syringe.

Resorting to numerous experiments, however, which we always conducted under the same conditions, we came up with some significant mean values. Besides, we carried out experiments to measure the quantity of hydrazine that can evaporate from the needle of the microsyringe during injection, and we discovered that most of the time this quantity can be ignored.

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